Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica B 345 (2004) 6–10
PHYSICA B
www.elsevier.com/locate/physb

Resonant X-ray scattering as a probe of the valence and magnetic ground state and excitations in $Pr_{0.6}Ca_{0.4}MnO_3$

S. Grenier[a,b,*], K.J. Thomas[a], Young-June Kim[a], J.P. Hill[a], Doon Gibbs[a], V. Kiryukhin[b], Y. Tokura[c], Y. Tomioka[c], D. Casa[d], T. Gog[d], C. Venkataraman[d]

[a] *Physics Department, Brookhaven National Laboratory Upton, NY 11973, USA*
[b] *Physics Department, Rutgers, State University of New Jersey, Piscataway, NJ 08854, USA*
[c] *Joint Research Center for Atom Technology (JRCAT), Tsukuba, Japan*
[d] *CMC-CAT, Advanced Photon Source, Argonne National Laboratory IL, USA*

Abstract

X-ray resonant techniques have been used to study the ground state and electronic excitations of the perovskite $Pr_{0.6}Ca_{0.4}MnO_3$. We utilized resonant diffraction at the Mn K-edge as a contrast technique for determining the pattern of Mn atoms in inequivalent crystallographic sites. In order to determine the important properties of the 3d electrons in this system, we have probed the unoccupied 3d orbitals using the magnetic and non-magnetic soft X-ray diffraction at the Mn L-edges. Finally resonant inelastic X-ray scattering experiments have been performed at the Mn K-edge. This latter technique provides new insights into the ground state as it probes the elementary electronic excitations.
© 2003 Published by Elsevier B.V.

PACS: 61.10.; 75.10.; 71.20.

Keywords: Half-doped manganite; Resonant X-ray diffraction; Inelastic X-ray scattering

1. Introduction

Resonant X-ray scattering (RXS) techniques have developed rapidly as energy-tunable and intense X-ray beams are now exploited in ever-increasing ways. We consider here two techniques that involve tuning the incident energy of a monochromatized beam through an atomic absorption edge. One may measure the modulation of the Bragg peak intensity with energy and one may energy resolve the inelastically scattered photons. The former technique is referred to as resonant X-ray diffraction (RXD), the latter is referred to as resonant inelastic X-ray scattering (RIXS).

Both the techniques are of great interest for the study of the ground states of strongly correlated electron materials: RXD is sensitive to the electronic configuration of the resonant element which includes the surrounding structural configuration and its symmetries, the highest occupied orbitals and their magnetic moments [1–3]. RIXS permits one to probe the lowest intra-site or inter-site electronic excitations such as charge transfer excitations or orbital excitations [4–6].

These resonant scattering techniques found natural applications in several 3d systems such as

*Corresponding author. Physics Department, Brookhaven National Laboratory Upton, NY 11973, USA.
E-mail address: grenier@bnl.gov (S. Grenier).

0921-4526/$ - see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/j.physb.2003.11.008

the high T_c cuprates, the magneto-resistive manganites and other systems of theoretical and technological importance. In these strongly correlated systems, the interplay among the various electronic degrees of freedom, including those of spin, charge, lattice and orbital degeneracy lies at the heart of the wide variety of phenomena. Particularly noteworthy examples of this interplay occur in the perovskite manganites $RE_xAE_{1-x}MnO_3$ (where RE is a trivalent rare earth and AE a divalent alkaline earth) for which the Mn atoms have a partially filled, high spin, 3d band. These materials exhibit rich phase diagrams in which the balance between the various degrees of freedom may be altered by a variety of methods, including hole doping, cationic size mismatch, temperature, pressure, magnetic field and electromagnetic radiation [7,8].

The ground state in the vicinity of half doping ($x = 0.5$) is interesting as an example of the balance among the various degrees of freedom because it exhibits the colossal magneto-resistant (CMR) effect. It has been believed to exhibit charge, orbital and magnetic order. In the 1950s, Goodenough described the ordering as comprising a checkerboard pattern of Mn^{3+} and Mn^{4+} sites (charge order) [9]. In this picture, the Mn^{3+} sites have an extra e_g electron that occupies a $3z^2 - r^2$-type orbital and these orientationally align in a cooperative manner to form an anti-ferro-type pattern within the plane (orbital order). On the basis of the exchange pathways set up by this order, a complex magnetic ordering occurs which may be thought of as zig-zag chains of ferromagnetically aligned spins which are coupled antiferromagnetically with their neighboring chains (CE-type AF order).

This simple picture has survived relatively unchallenged to the present day. The support from experimental observations includes the various structural studies (both X-ray and neutron) which reveal the presence of inequivalent Mn sites, one of which sits in a distorted octahedron consistent with $3z^2 - r^2$ occupancy, the other in an undistorted octahedron (see e.g. [10]). In addition, neutron refinement of magnetic moments find two different moments on the two sites, with $\mu(3+)/\mu(4+)$ about 1.1 [11]). Further consistency is found with recent RXS results which identify short-range orbital correlations as the origin of the observed short-range magnetic correlations on the Mn^{3+} sublattice [10,12]. Finally, transport, optical and NMR data have all been interpreted in terms of this picture [7].

However, the existence of this Mn valence organization has been recently questioned. In particular, a complete valence separation (i.e. Mn^{3+}/Mn^{4+}) appears to be inconsistent with X-ray absorption near edge structure spectra [13]. This study suggests that, at most, only a small charge disproportionation, either on the manganese atoms or at a molecular scale, can be supported [13]. Further, the recent crystallographic structure refinement of Daoud-Aladine et al. [14] is inconsistent with a checkerboard model of inequivalent Mn atoms, it exhibits no significant charge disproportionation and serves as a basis for introducing a model based on the so-called Zener polarons. Though this latter study was questioned [15], both reveal that despite 50 years of experimental and theoretical effort, there remain some very basic questions to be answered in the half-doped manganites.

We have sought to address this issue by performing RXD studies at the Mn K- and L-edges and RIXS at the Mn K-edge of $Pr_{0.6}Ca_{0.4}MnO_3$.

2. RXD at the Mn K-edge and L-edge

The X-ray resonant scattering process may be described as the virtual absorption of a photon by a core electron that is promoted to an unocuppied level. The excited electron decays to the initial state thereby emitting the outgoing photon, without loss of energy in the case of elastic scattering. The unoccupied states are sensitive to the electronic configuration, such as the population of the highest occupied orbitals, their magnetic moment and the surrounding atomic distribution. As a result, the transition rate and therefore the X-ray resonant cross-section are also sensitive to such quantities.

The process is to a good approximation "dipolar" in that only electronic states whose

angular momenta are separated by one unit can be coupled. Therefore the interesting valence Mn 3d states, are accessible in principle only from the 2p or 3p bands. This has an important consequence from an experimental point of view, because the energy of these resonances limits the accessible Q space (the 2p edges are about 650 eV which corresponds to $\lambda \approx 19$ Å for the photons). Furthermore at such energies, the absorption along the beamline is important, so all the set up including the spectrometer, the detector and the cold finger of the cooling system need to be in vacuum. An alternative approach has been to study the 3d structure indirectly with K-edge RXD.

At the K-edge one promotes the 1s electron to an unoccupied 4p level, which are mostly sensitive to the oxygen configuration. Therefore the RXD technique at the K-edge is mainly used as a contrast technique. Indeed different crystallographic sites have different resonant scattering factors because of different surrounding oxygen configuration. In Fig. 1, one can see the strong variations in the diffracted intensity for the (3 0 0) and (0 3 0) reflections, for which two inequivalent sites scatter in opposite phase. Tuning to the K-edge enhances this difference. The analysis of these measurements indicates that inequivalent Mn atoms are arranged in a checkerboard pattern (thus supporting the CE-type model) [15]. The spectra have been measured at 9IDB (Advanced Photon Source, USA).

The orbital and magnetic ordering in $Pr_{0.6}Ca_{0.4}MnO_3$ has been studied also at the L-edges. At X1 beamline (National Synchrotron Light Source, USA) we have measured the energy lineshape of the orbital $(0\,\frac{1}{2}\,0)$ and magnetic $(\frac{1}{2}\,0\,0)$ propagation vectors respectively [16]. At the L_{II} and L_{III} edges one can directly access the unoccupied 3d states. The dimension of the orbital and magnetic unit cells, each about 11 Å, makes diffraction possible at these energies. The resonant scattering factors now have a strong magnetic contribution due to the anti-ferromagnetic ordering of the occupied 3d states. We have also characterized the temperature dependance of the magnetic and orbital orderings. The results will be presented elsewhere [16].

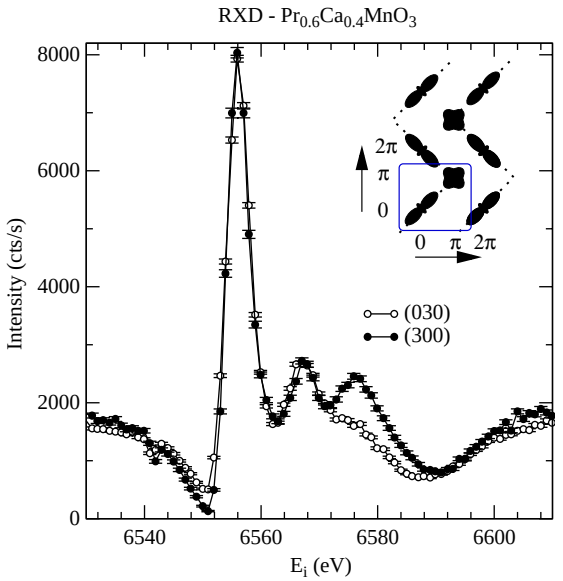

Fig. 1. RXD at the (3 0 0) and (0 3 0) reflections show similar resonant behavior as the propagation vectors for inequivalent Mn atoms are equivalent along the (1 0 0) and (0 1 0) crystallographic directions. The real space model and the crystallographic phase shift between the two sites for these reflections are indicated in the inset [15].

3. RIXS at the Mn K-edge

By tuning the energy of the incident photons through the Mn absorption edge, one can observe two new types of scattering process. The first of these corresponds to a one-electron decay of the core hole, from an electron state below the Fermi energy. The decay $3d \rightarrow 1s$ is such a process; the corresponding $K\beta_5$ line at 6.534 keV is shown in Fig. 2. The second process involves an energy transfer from the virtual 1s–4p exciton to the valence electron system. When the exciton decays, the photon is emitted with an energy equal to the initial energy minus the energy transfer to the valence electrons. Such scattering is responsible for the intensity visible in Fig. 2 between about 2 and 15 eV energy loss.

In principle the scattered photons can be measured over the entire Q space at the K-edge, so that the entire Brillouin zone is accessible. In Fig. 3 we also show new data of the momentum dependence of the "11.5 eV" emission line. The excitation spectra have been fitted to a Lorentzian:

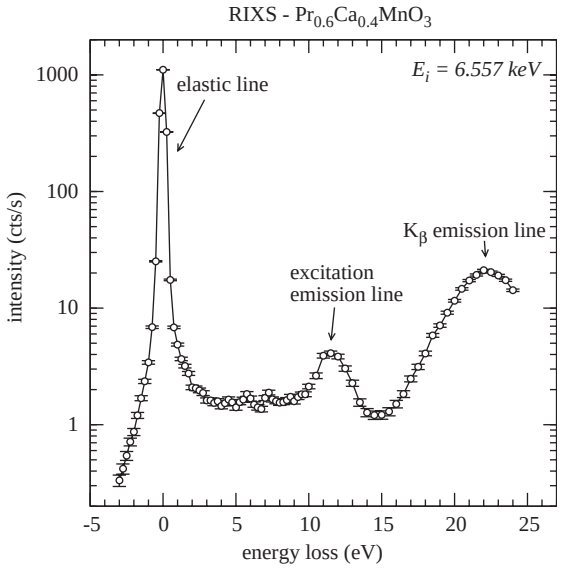

Fig. 2. RIXS spectrum of $Pr_{0.6}Ca_{0.4}MnO_3$ which shows the intensity of the scattered photons as a function of the energy loss $E_i - E_f$. The incident photon energy was 6.557 keV.

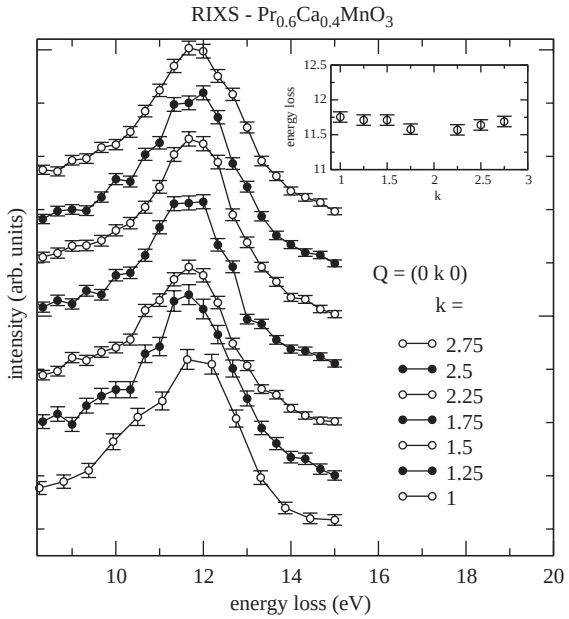

Fig. 3. Momentum dependence of the "11.5 eV" feature, the inset shows the energy of that excitation as a function of $Q = (0k0)$. The incident energy was $E_i = 6.557$ keV.

the position in energy of the emission line is confined between 11.57 and 11.75 eV (± 0.075 eV). The momentum dependence is small and appears symmetric with respect to the (0 2 0) position with maxima at the (0 1 0) and (0 3 0) positions. We note that the position in the Brillouin zone is not well defined as this 3D perovskite crystallizes in different domains corresponding to the (0 1 0), (1 0 0) and (1 1 2) crystallographic directions. Though as the momentum dependence indicates a non-local excitation, these data can shine new light on the interpretation of this excitation. Up to now it has been attributed to the charge transfer from the 2p oxygen band to the Mn 4s/4p-band [17].

4. Conclusion

Resonant scattering techniques at the K-edge and the L-edges have been performed to study the ground state and the low-energy excitation spectrum of $Pr_{0.6}Ca_{0.4}MnO_3$. The RXD analysis at the K-edge supports a checkerboard pattern of inequivalent Mn atoms. We expect that the analysis of the magnetic and orbital RXD spectra at the L-edges and of RIXS data will lead to a quantitative description of the occupied 3d states in an unprecedented detail. To our knowledge, the half-doped CMR $Pr_{0.6}Ca_{0.4}MnO_3$ is the only system for which all these measurements are available.

Acknowledgements

Use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Brookhaven National Laboratory is supported under DOE Contract No. DE-AC02-98CH10886. Support from the NSF MRSEC program, Grant No. DMR-0080008, is also acknowledged.

References

[1] M. Blume, in: G. Materlik, C.J. Sparks, K. Fischer (Eds.), Resonant Anomalous X-Ray Scattering, Theory and Applications, North-Holland, Amsterdam, 1994.

[2] D.H. Templeton, L.H. Templeton, Acta Crystallogr. A 36 (1980) 237.
[3] D. Gibbs, D.E. Moncton, K.L. D'Amico, J. Appl. Phys. 57 (1985) 3619.
[4] A. Kotani, S. Shin, Rev. Mod. Phys. 73 (2001) 203.
[5] C.C. Kao, W.A.L. Caliebe, J.B. Hastings, J.-M. Gillet, Phys. Rev. Lett. 54 (1996) 16361.
[6] J.P. Hill, C.C. Kao, W.C. Caliebe, M. Matsubara, A. Kotani, J.L. Peng, R.L. Greene, Phys. Rev. Lett. 80 (1998) 4967.
[7] T.A. Kaplan, S.D. Mahanti, Physics of Manganites, Kluwer Academic, Dordrecht, New York, 1999.
[8] M.B. Salamon, M. Jaime, Rev. Mod. Phys. 73 (2001) 583.
[9] J.B. Goodenough, Phys. Rev. 100 (1955) 564.
[10] P.G. Radaelli, D.E. Cox, M. Marezio, S.-W. Cheong, Phys. Rev. B 55 (1997) 3015.
[11] Z. Jarák, S. Krupicka, Z. Simsa, M. Dlouhá, S. Vratislav, J. Magn. Magn. Mater. 53 (1985) 153.
[12] M.V. Zimmermann, C.S. Nelson, J.P. Hill, D. Gibbs, M. Blume, D. Casa, B. Keimer, Y. Murakami, C.-C. Kao, C. Venkataraman, T. Gog, Y. Tomioka, Y. Tokura, Phys. Rev. B 64 (2001) 195133.
[13] J. García, M.C. Sánchez, G. Subías, J. Blasco, J. Phys.: Condens. matter 13 (2001) 3229.
[14] A. Daoud-Aladine, J. Rodriguez-Carvajal, L. Pinsard-Gaudart, M. Fernández-Díaz, A. Revcoleschi, Phys. Rev. Lett. 89 (2002) 097205.
[15] S. Grenier, J.P. Hill, D. Gibbs, K.J. Thomas, M.V. Zimmermann, C. Nelson, Y. Tokura, Y. Tomioka, D. Casa, T. Gog, C. Venkataraman, Resonant X-ray diffraction study of the magnetoresistant perovskite $Pr_{0.6}Ca_{0.4}MnO_3$, cond-mat 0305216.
[16] K.J. Thomas, J.P. Hill, Y.-J. Kim, S. Grenier, P. Abbamonte, L. Venema, A. Rusydi, Y. Tomioka, Y. Tokura, D.F. McMorrow, M. van Veenendaal, cond-mat/0311553.
[17] T. Inami, T. Fukuda, J. Mizuki, S. Ishihara, H. Kondo, H. Nakao, T. Matsumura, K. Hirota, Y. Murakami, S. Maekawa, Y. Endoh, Phys. Rev. B 67 (2003) 045108.